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Rearrangement of Alkyl Amines Ethyl Aniline

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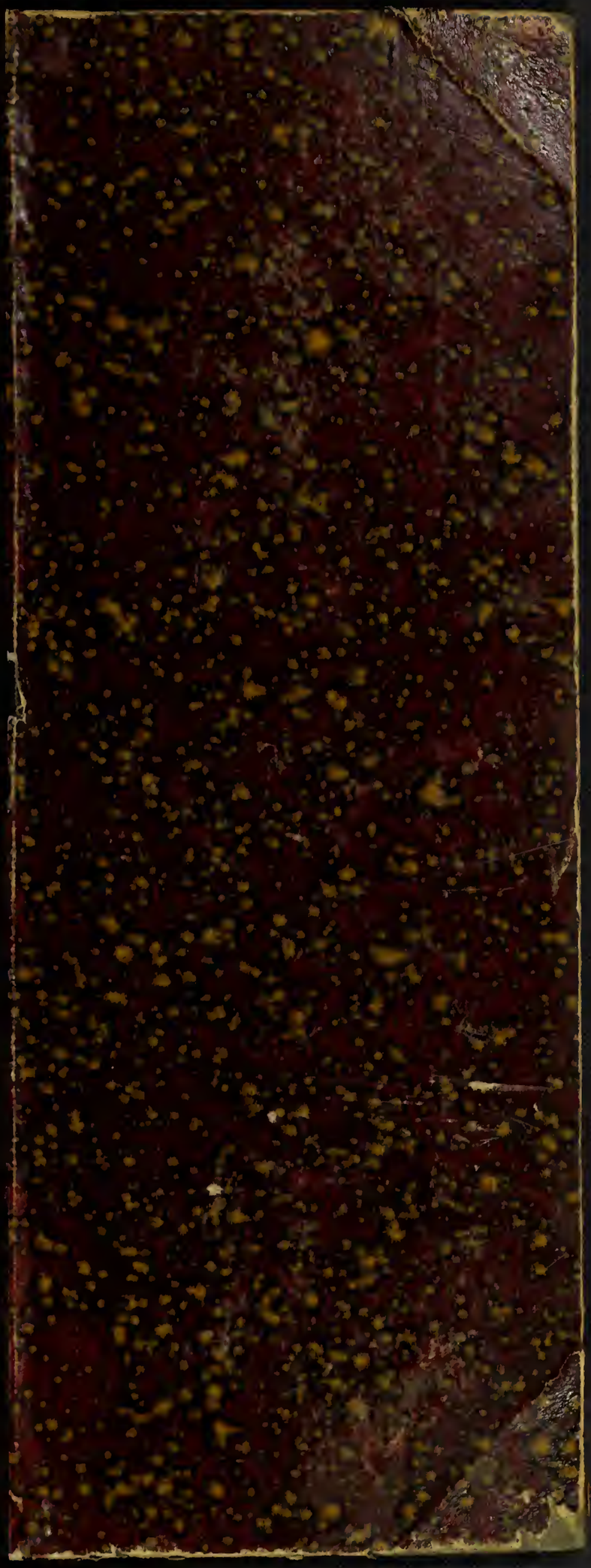

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REARRANGEMENT OF ALKYL AMINES
ETHYL ANILINE

BY

CHARLES WILLIAM KNUDSEN

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMISTRY

COLLEGE OF SCIENCE

UNIVERSITY OF ILLINOIS

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June 5, 1913.

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

CHARLES WILLIAM KNUDSEN

ENTITLED Rearrangement of Alkyl Amines - Ethyl Aniline

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF BACHELOR OF SCIENCE IN CHEMISTRY.

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TABLE OF CONTENTS.

	Page
Introduction	1
History	1
Theory	3
Experimental	3
Introduction	3
Determination of Primary Amine	5
Aniline	5
Amino-ethyl-benzene	6
Determination of Secondary Amine	7
Ethyl aniline	7
Separation and Determination of Primary, Secondary, Tertiary and Quaternary Amines.	8
Separation of Quaternary Amine	8
Separation of Primary, Secondary and Tertiary Amines	8
Summary	9
Rearrangement	10
Experiment No. 1 --Ethyl aniline	10
Experiment No. 2 --Ethyl aniline hydrochloride	10
Experiment No. 3	12
Summary and Conclusions	13

THE REARRANGEMENT OF ALKYL AMINES.

INTRODUCTION.

Practically all that is known of the rearrangement of ethyl aniline is due to A. W. Hofman. In 1870 this noted German chemist published a series of articles in "Die Berichte der Deutschen Chemischen Gesellschaft" on the subject of the rearrangement of alkyl amines.

Little has been done since then and still less has been published concerning the reaction, its mechanism, or its control. Hofman failed to isolate and identify many of the products of the reaction or to explain its mechanism. The questions arising concerning its mechanism are: Is it an inter- or an intra-molecular reaction and at what stage does the rearrangement occur? But before either of these questions can be settled definitely, a method for the separation of the amine products must be devised.

This work was undertaken with the end in view of devising a quantitative separation of the four classes of aromatic amines and of determining at what stage the rearrangement took place.

HISTORY.

Hofman (1) prepared the water free hydrochloride of ethyl aniline by passing dry hydrochloric acid gas into a pure preparation of ethyl aniline. He then heated this compound in a sealed tube for three hours and obtained a brown, honey like sirup. No report is made of the probable composition of this product. The same sirupy

mass was heated again at a temperature of 300°-330° C. for twelve to eighteen hours and at the end of this time was changed to a crystalline mass. Hofman separated the bases with alkali. The products were not secondary bases but were called amino-ethyl-benzenes, no reference being made to the position of the ethyl groups. Sulphuric acid formed a crystalline compound with the products which was not easily soluble, and a beautifully crystalline salt was formed with chlorplatinic acid.

The extract from the alkaline solution distilled for the most part at 212°- 216° C., but there were other higher boiling bases. From an analysis of the platinum salt and the quaternary compound formed with methyl iodide, Hofman showed that this particular base was an amino-ethyl-benzene. He also analyzed the compounds formed with chlorplatinic acid and the higher boiling fractions and found that the platinum content was reduced. This reduction was due to the presence of more than one ethyl group in the ring, or attached to the nitrogen. Beilstein and Kühlberg (2) had prepared an amino-di-ethyl-benzene and gave its boiling point at 213°- 214° C. Hofman concluded that this compound was identical with one of his higher boiling bases.

Hofman thought the reaction consisted simply in an exchange in position between the alkyl group in the amino group and a hydrogen atom in the ring. Results with methyl aniline similar to those obtained with ethyl aniline led Hofman to state (3) "There is no longer any doubt that the hydrogen of the phenyl group is replaced by a methyl group and that we have obtained a group of higher homologues of methyl aniline by this method". Several fruitless attempts were made to separate the bases by distillation. Similarly Hofman found it impossible to separate their salts by

crystallization.

Meyer and Jacobsen (4) refer to the rearrangement of Hofman's as a very important technical method for the preparation of the homologues of aniline, and it is well known that this method is generally used in the German dye-stuff industries for the preparation of amino-alkyl-benzenes.

THEORY.

It has been shown by Derick and Bornmann (5) that the rearrangement of di-acyl amines occurs to give compounds of a lower ionization constant. This difference between the ionization constant of the compound before and after rearrangement is quite marked. It was assumed in the work with the rearrangement of ethyl aniline that a similar relationship also held between the ionization constant of the compound before and after rearrangement. For example, suppose amino-ethyl-benzene, the rearranged product obtained. To fit the hypothesis it is necessary to assume that the original compound had a considerably larger ionization constant. The hydrochloride of ethyl-amino-benzene is the original compound, whose ionization constant differs little from that of the rearranged compound. It is probable then, that some intermediate product is formed with a larger ionization constant before the rearrangement occurs, and this intermediate product is assumed to be the quaternary compound.

EXPERIMENTAL.

Introduction.

As previously stated a method for the separation of the four classes of aromatic amines was necessary in order that the

products of the reaction could be separated. Up to the present time the method of Hinsberg (6) is the best for such a quantitative separation.

A mixture of the four classes of aromatic amines is made alkaline and subjected to steam distillation. The quaternary compound is not volatile in steam, the other three classes are usually volatile. In case they are not they may be removed from the quaternary by an ether extraction. All the primary, secondary and tertiary ethyl anilines known are volatile in steam. The quaternary compound is therefore determined by a method of difference.

The mixture of primary, secondary and tertiary amines is then treated with benzene sulphonyl chloride in a solution of potassium hydroxide. The following reactions occur:

$$C_6H_5\text{-}N\langle^{H}_{H} + Cl\text{-}SO_2\text{-}C_6H_5 = C_6H_5\text{-}N\langle^{H}_{SO_2\text{-}C_6H_5} + HCl$$

$$C_6H_5\text{-}N\langle^{H}_{SO_2\text{-}C_6H_5} + KOH = C_6H_5\text{-}N\langle^{K}_{SO_2\text{-}C_6H_5} + H_2O$$

This potassium salt is soluble in alkaline solution.

$$C_6H_5\text{-}N\langle^{R'}_{H} + Cl\text{-}SO_2\text{-}C_6H_5 = C_6H_5\text{-}N\langle^{R'}_{SO_2\text{-}C_6H_5} + HCl$$

This product is insoluble in alkali or water but is soluble in ether.

The tertiary amine forms no compound with benzene sulphonyl chloride. It is interesting to note that no dye is formed with the tertiary di-ethyl aniline as is formed with the tertiary di-methyl aniline.

If the alkaline mixture is now extracted with ether, the sulphone derivative of the secondary amine, and the tertiary amine are removed. Then by adding to this ether extract a hydrochloric

acid solution, the hydrochloride of the tertiary amine forms and precipitates from the ether. The ether layer is removed and evaporated and the derivative of the secondary amine thus obtained. The water layer is made alkaline, extracted with ether and the tertiary amine obtained.

By making acid the solution which contains the potassium salt of the mono-sulphonic amide, the amide is set free and may be extracted with ether.

Hinsberg followed this scheme for the quantitative separation of a number of amines and was able to obtain yields above 90% of the theoretical amounts. This seemed then to be the most advisable method for use in the present investigation.

Determination of Primary Amine.

Aniline.

A number of quantitative determinations were made with known amounts of aniline. The first determinations were made according to Noyes and Mulliken(7) and the yields were much below theoretical. A number of typical analyses are given

Wt. aniline	0.55 gm.	Wt. derivative	1.00 gm.	% Theory	71.9
" "	0.55 "	" "	1.10 "	"	79.1
" "	0.65 "	" "	1.10 "	"	67.5

Since amounts of benzene sulphonyl chloride were used in excess, and heat and time were given the reacting mixture there was no doubt that the aniline went into combination with this reagent. An ether extraction of the alkaline mixture was always made to remove any unused benzene sulphonyl chloride that might be present, but no account had been taken of it. Since the yields were so low this extract was examined and it was found that on drying over anhydrous sodium sulphate and evaporating the ether, a pretty white

crystalline product was obtained that melted sharply at 108.5°. This product was the derivative of the primary amine that had been lost in previous determinations. It was quite evident that hydrolysis of the salt had occurred and that the following reaction had taken place.

$$C_6H_5\text{-}N\langle^{K}_{SO_2\text{-}C_6H_5} + HOH \rightleftharpoons C_6H_5\text{-}N\langle^{H}_{SO_2\text{-}C_6H_5} + KOH$$

It also became quite evident that by an application of the principle of mass action, an increase in the concentration of the alkali would drive back hydrolysis and prevent the extraction of the free amide with ether. Experiments were made with potassium hydroxide of various concentrations with the result that with an increase in concentration of alkali used, the amount of the ether extract from the alkali was diminished proportionally. Saturated, or nearly saturated, potassium hydroxide, proved to work satisfactorily and good results were obtained. A few analyses are given.

Wt. Sample.	Wt. Derivative	% Theory	Wt. ether extract
1.01 gms.	2.41 gms.	96.4	------
1.00 "	2.33 "	93.2	------
1.00 "	2.60 "	100.0	.09

In the last case there was evidently some unchanged benzene sulphonyl chloride left and removed by ether extractions; hence the high result. These were careful determinations but mechanical difficulties seemed to prevent better separations.

Amino-ethyl-benzene.

According to Hofman amino-ethyl-benzene is a product in this rearrangement, so determinations were made of it just as in the case of aniline.

Preparation of sulphone derivative.-- The compound formed when para-amino-ethyl-benzene is treated with benzene sulphonyl

chloride is not described in the literature. Para-amino-ethyl-benzene was prepared by the reduction of the corresponding para-nitro-ethyl-benzene. An excess of benzene sulphonyl chloride was added and the mixture was well shaken with saturated potassium hydroxide solution. Some heat was evolved by the reaction. The mixture was cooled and extracted with ether. The ether would remove any unchanged aniline or benzene sulphonyl chloride or di-sulphone derivative that might be formed. Only the potassium salt of the amide would remain. The alkaline solution was then made acid and extracted with ether, the extract dried over anhydrous sodium sulphate and evaporated. A crystalline product was obtained that appeared like the sulphone derivative of aniline. This was recrystallized from alcohol, and dried over a porous plate. Three melting points were taken. The melting point found was 55° C.(uncorrected).

Determination.-- The determination of amino-ethyl-benzene was made exactly like that of aniline. There seemed to be a tendency toward too high results with this compound. This may have been due to the formation of the di-sulphone derivative but time did not permit its investigation. The results of some careful determinations are given.

Wt. amino-ethyl-benzene.	Wt. of Derivative.	% Theory.
0.50 gms.	1.09 gms.	100.+
0.50 "	1.03 "	96.

Determination of Secondary Amine.

Ethyl aniline.

The reaction with ethyl aniline was next tried. Little difficulty was met with here provided the reaction went long enough for the potassium hydroxide to decompose the excess benzene sulphonyl chloride. The product obtained was dried in a current of air until

no further decrease in weight occurred. This same practice was used in all determinations. Two analyses are as follows:

Wt. Ethyl aniline.	Wt. Derivative.	% Theory
0.5 gm.	1.00 gm.	92.6
0.5 "	1.02 "	94.4

Separation and Determination of Primary, Secondary, Tertiary and Quaternary Amines.

Separation of Quaternary Amine .

A mixture of the four amines, para-amino-ethyl-benzene (primary), ethyl aniline (secondary), di-ethyl aniline (tertiary), and tri-ethyl-phenyl-ammonium iodide, was subjected to steam distillation to determine how complete a separation of the quaternary compound could be made from the other three classes of amines and to determine how much time was necessary for the separation. Steam was passed through a mixture of a gram each of the above compounds for thirty minutes. The distillate measured about 200 cc. and the weight of the recovered amines was practically 3 grams or a theoretical recovery.

Separation of Primary, Secondary and Tertiary Amines.

Separations were then made of primary, secondary, and tertiary amines. A mixture of 0.5 gm. each of these amines was treated with an excess of benzene sulphonyl chloride and 25 cc. of saturated potassium hydroxide solution added to each of two samples taken for analysis. The mixtures were shaken until the odor of the benzene sulphonyl chloride disappeared. The method was then completed as described before and each of the derivatives (or recovered amines) dried for 20 minutes in a dry air current.

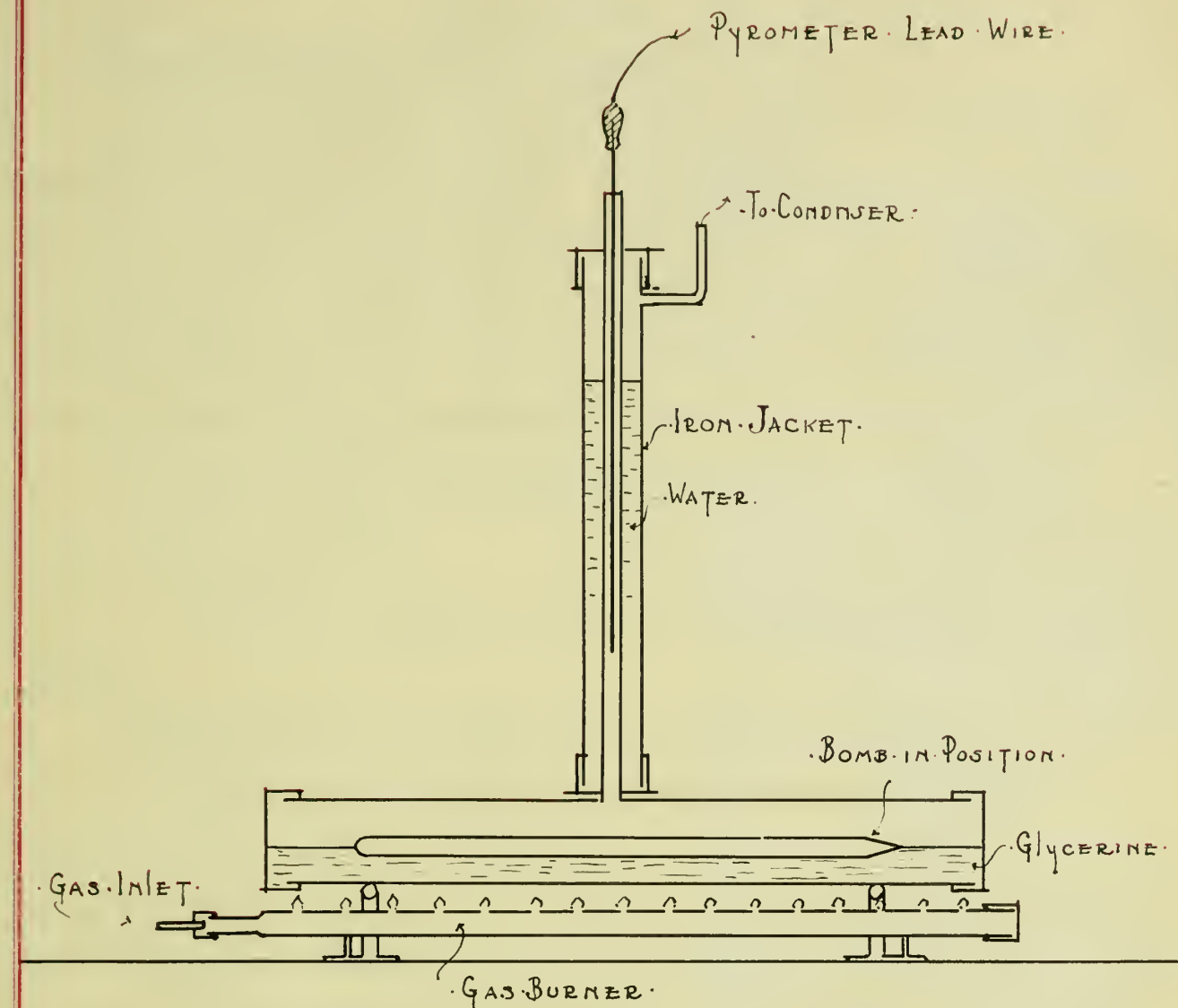
The results of two analyses are as follows:

No. 1.	Wt. sample.	Wt. derivative or recovered product.	% Recovery.
Ethyl aniline	0.50 gm.	0.90 gm.	83
Di-ethyl aniline	0.50 "	0.45 "	90
Aniline	0.50 "	1.25 "	100
No. 2.			
Amino-ethyl-benzene	0.50 "	1.00 "	93
Ethyl aniline	0.50 "	1.15 "	100+
Di-ethyl aniline	0.50 "	.45 "	90

The second determination agrees more nearly with the results obtained on analyses of the individual members of the mixtures. The primary amine is high in the first, due probably to an imperfect extraction. The results in the second determination indicate again that some of the di-sulphone derivative is formed from the primary amine which is extracted with the derivative of the secondary amine.

Summary.

The results obtained by this method of separation show that with careful manipulation the method is accurate to about five per-cent. Hofman stated that a whole series of homologues of the original amine might be obtained in the rearrangement and if such is true, this method will serve only for classes of amines and not specific members of the series of rearranged products. In case, however, the reaction instead of being one of intramolecular nature is an intermolecular reaction in which two molecules of ethyl aniline react to give one of aniline and one of di-ethyl aniline, the method will serve admirably. And, if the reaction is one of rearrangement, it will be possible to determine (by the amount of primary amine formed) at what temperature the reaction takes place to any



Special Bomb

- Furnace -

appreciable extent.

Rearrangement.

Experiment No. 1 --Ethyl Aniline.

A bomb containing 25 cc. of ethyl aniline was heated in a sealed glass tube in the special furnace (see Figure) for 6 hours at 280°. After cooling the bomb was removed. There was no change in appearance of the contents. The tube opened with little pressure. The isocyanide test was made on the sample for primary amines. The test was negative. An analysis was run on the sample.

Wt. sample.	Wt. derivative of secondary amine.	% recovery.
2.05 gm.	4.30 gm.	97+

It is safe to conclude then that no reaction had taken place.

Experiment No. 2. --Ethyl Aniline Hydrochloride.

A sealed glass tube containing 5 grams of ethyl aniline hydrochloride (prepared by passing dry hydrochloric acid gas into an ether solution of recently purified ethyl aniline) was heated in the furnace for six hours at a temperature of 280°- 290°C. The contents changed from a snow white solid to a brown looking mass, partly crystalline, partly sirupy. The bomb opened with little pressure. A very foul odor was noticeable.

Treatment of Bomb Contents:-- The contents of the glass tube were extracted with ether, the extract dried, the ether evaporated and the residue weighed. This extract was a brown, viscous, foul smelling liquid --weight 0.11 gram.

The residual content of the bomb was made alkaline and subjected to steam distillation for two hours, much longer than had been required in previous experiments with amines. The distillate was

saturated with sodium chloride, extracted with ether and the ether extract dried over anhydrous sodium sulphate and evaporated. The weight of amines thus obtained was 1.80 grams. A dark brown, heavy oil remained back in the container and six hours of steam distillation was without action upon this oil.

The amines were then analyzed according to the method already described. The products in each case were dried in a dry air current for one hour to remove all ether. The results of the analysis

Wt. sample of amines.		Wt. derivative.		% Recovery.
No. 1	1.00 gm.	Primary	1.85 gm.	85
		Secondary	.30 "	13
		Tertiary	nil.	--
No. 2.	0.61 "	Primary	1.06 "	81
		Secondary	.20 "	15
		Tertiary	nil.	

In calculating these percent yields it was assumed that the primary amine was amino-ethyl-benzene, the secondary amine of course being ethyl aniline.

The derivative of the primary amine was a pretty,white, crystalline compound, not unlike the sulphone derivative of aniline in appearance. Some of it was purified by recrystallization from alcohol, dried on porous plate and its melting point taken. The melting point was not at all sharp. The compound showed signs of softening at 110° and did not liquefy entirely until a temperature of 135° was reached.

It is evident from this experiment that the reaction is not simply an intermolecular one between two molecules of ethyl aniline. If such were the case the melting point of the derivative would be that of the sulphone derivative of aniline,viz., 108.5°C., and also di-ethyl aniline would be present in the same molar quantity as aniline. It is evident, however, that a rearrangement has occurred

giving a primary amine (or amines). That this primary amine does not consist of para-amino-ethyl-benzene is shown by the melting point of its purified sulphone derivative. Had para-amino-ethyl-benzene been the only primary amine present the melting point of the sulphone derivative would have been 55°C. The long range of temperature during melting is evidence that a mixture of primary amines is present.

Experiment No. 3.

A duplicate experiment was made with seven grams of ethyl aniline hydrochloride with the exception that the heating was prolonged to ten hours at 280°-300°C. The separation of the products was qualitative. Much primary amine (or amines) was present whose sulphone derivative was carefully crystallized from alcohol. A melting point of this substance was 78° (uncorrected). This melting point is about midway between that of the sulphone derivative of para-amino-ethyl-benzene (55°) and that of aniline (108.5°). It would seem then that there was a possibility of the mixture of primary amines consisting of nearly equal parts of aniline and para-amino-ethyl-benzene. If such is the case there is evidence that a reaction has taken place that is both intermolecular and intramolecular, and one could expect a tertiary amine to be present. There was no tertiary amine in the steam distillate, therefore no di-ethyl aniline was found in the reaction. If a tertiary amine is formed it must remain back in the containing flask and is not volatile in steam.

Treatment of non-volatile residue:-- The residue remaining back in the containing flask was a viscous, heavy oil of very dark color. The test for primary amines by means of the phenyl iso-nitrile reaction was negative. Enough of this oil was obtained

to be used successfully in a Mulliken's boiling point apparatus (8). The oil became less viscous at higher temperatures but did not boil under 315° C. (uncorrected). An analysis showed nitrogen.

Should this non-volatile oil prove to be a tertiary amine, there is little doubt that an intermolecular reaction has occurred as well as a rearrangement. Time did not permit further investigation.

SUMMARY AND CONCLUSIONS.

Hofman(9) used quantities of the hydrochloride of the amine as large as 10 kilograms in some of his experiments. Only a few grams were used in the experiments in this case. There is little doubt had larger quantities been used a better separation of the products of the reaction could be obtained for it was found that a mixture of primary amines was formed and the benzene sulphonyl chloride reaction serves only to separate classes of amines. By working on larger quantities, the sulphone derivatives of the primary and secondary amines would be sufficient in amount to yield quantities of primary and secondary amines on decomposition that could be further separated by distillation.

In these preliminary experiments the temperature at which a rearrangement occurs can be more accurately obtained by using small quantities of the hydrochloride in the special furnace.

The use of benzene sulphonyl chloride as a reagent for the separation of the four classes of amines met with in this series of experiments, with careful manipulation and with the use of saturated potassium hydroxide solution, is quite practicable within an accuracy of five percent.

There is evidence that a di-sulphone derivative is formed with the primary amine as well as a mono-substituted derivative.

This will interfere in the determination.

That a rearrangement occurs is shown by the formation of primary amines other than aniline, and if the non-volatile product should prove to be a tertiary amine, there is evidence of an intermolecular reaction.

Since the only ethyl- and ethyl-amino-ethyl benzenes known and characterized are ortho-, meta- and para-amino-ethyl-benzene, 1-3-di-ethyl-amino-benzene (?), ethyl aniline and di-ethyl aniline, there is a need for some synthetic work on other members of the series, and on their characteristics before the problem of the rearrangement of ethyl aniline hydrochloride can be rightly attacked.

Ethyl aniline does not rearrange at 280°-300° C. The hydrochloride of the same compound will rearrange at this temperature.

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